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MODERN PROBLEMS OF OBTAINING HIGH-TRANSPARENCY GLASSES

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The conditions for obtaining high-transparency glasses are examined. Data on the effect of coloring impurities and additives on the optical and spectral properties of glasses are presented. The role of rare-earth elements and the prospects for using new materials and technologies in the production of articles from high-transparency glasses are shown.

Key words: glass, light-transmission, impurities, color tones.

To obtain high-transparency colorless glass it is important to use high-quality raw materials and coloring iron impurities must be put into the maximally oxidized state with color-tone compensation and minimum reduction of light transmission [1 – 3]. The methods of solving this problem are different in each concrete case.

High transparency can be attained not only by using high-quality raw materials but also by choosing a definite composition of the glass. The composition and raw materials are intimately correlated. In addition, oxidative conditions must be maintained at all stages of glassmaking.

To produce high-grade and crystal glass the basic composition of the glass must be such that the required properties are obtained — high light-transparency, refractive, whiteness, and brightness indices — and the technological properties must match the glassmaking and output method.

The compositions of high-grade and crystal glasses are wide-ranging in both the lead-silicate and sodium-calcium-silicate systems. The compositions include zinc, barium, lanthanum, zirconium, and boron oxides, which have a positive effect on the above-indicated properties of glass.

The PbO content in commercial compositions of crystal glasses varies over a wide range (from 0 to 32%[2]).

To develop low-lead and lead-free compositions the index of refraction n_d is taken as the most important assessment criterion in the normative documentation. The effect of different oxides on the change of the refractive index in lead-silicate glasses is shown in Fig. 1. It is evident that among oxides the partial contribution of CaO is highest, followed by B_2O_3, ZnO, and BaO and additives such as ZrO_2 and La_2O_3 [4]. For this reason, to develop new crystal-glass compositions preference is given to these oxides. Crystal glass must have not only a high index of refraction but also high light-transmission without tones in the visible part of the spectrum.

In the opinion of the leading manufacturers of foreign crystal glass, the high degree of “aging,” i.e., the change of the color tone with time under the action of sunlight, makes Russian crystal glass less competitive on the world market. This is due to the elevated content in the glass of polyvalent metal coloring impurities, especially iron oxides.

The content of iron oxides in some foreign and Russian glasses produced commercially is presented in Table 1.

Comparing the data presented in the Table 1 shows that the content of iron oxides in Russian commercial compositions is high compared with the foreign compositions. In ad-

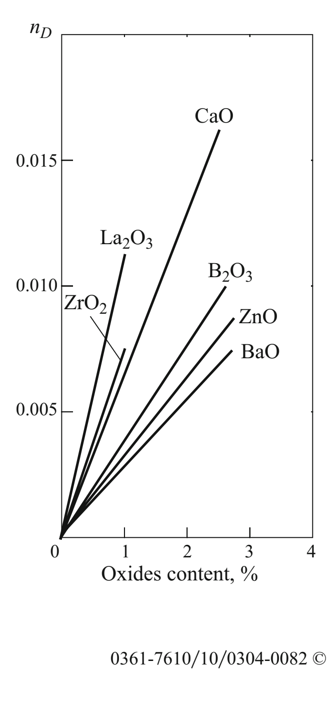

Fig. 1. Effect of different oxides on the index of refraction of glasses in the system K_2O – PbO – SiO_2 (PbO — 26%).

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[2] Here and below — content by weight.

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TABLE 1.

Glass type	Fe_2O_3 content, wt.%	
	Germany	Russia
Lead crystal	0.014	0.018 – 0.022
Potassium crystal	0.013	0.020 – 0.027
Colorless glass (high-grade)	0.025	0.025 – 0.040

dition, the impurity content in Russian glasses is characterized by a large spread, depending on the production methods and manufacturer.

It should be noted that aside from iron impurities different lead crystal and crystal glasses contain chromium impurities introduced by potash. Potash, in which the maximum admissible Cr_2O_3 content is 0.0007% (in the future 0.0005%) for glass and crystal glass, from commercial suppliers is contaminated with chromium oxide impurities by a factor of 1.5 – 3 higher than the indicated levels, which makes it practically impossible to decolorize glass.

Figure 2 displays spectral curves of crystal glasses containing chromium oxides. Maximum absorption in the short-wavelength (450 nm) and long-wavelength (650 nm) regions of the spectrum is characteristic for Cr^{3+} ions (curve *1*). The glass possesses high transmission at green wavelengths, so that it is characterized by a distinct greenish tone. In this case it is very difficult to obtain glass without any tones and with high light transmission. The decolorizing mixes using nickel oxide (see Fig. 2, curve *2*) as well as erbium and neodymium oxides (see Fig. 2, curve *3*) cannot completely cover the green tone due to the presence of chromium impurities. The spectral curves *2* and *3* even out somewhat as the visible-range light transmission decreases. The calculation of the color characteristics of these glasses with source *B* (daylight) shows a distinct green tone, characterized by the dominant wavelengths 566 and 568 nm with low light transmission 87.3 and 88.1%, respectively. Such light-transmission indicators lie at the level of container and sheet glass. For this reason, even though the index of refraction is high, such glass can be called crystal glass only conditionally.

A number of foreign manufacturers and specialists place colorlessness and light transmission of glass at the top of the list for assessing the quality of crystal glass and they consider that crystal glass can be so called only if it has no color tone. Examples are the Moser and Bohemian crystal glasses which are completely free of lead oxides.

In this connection a very important avenue for optimizing the composition of crystal glass is using the correct combination of oxides and appropriate raw materials for introducing them into the mix. Thus, to develop crystal glasses the K_2O content introduced by potash, which is expensive and at the same time contaminated with chromium impurities, can be reduced to a minimum, but then it will be necessary to change the basic composition of the glass and the raw materials used. It is important to preserve the presence of two

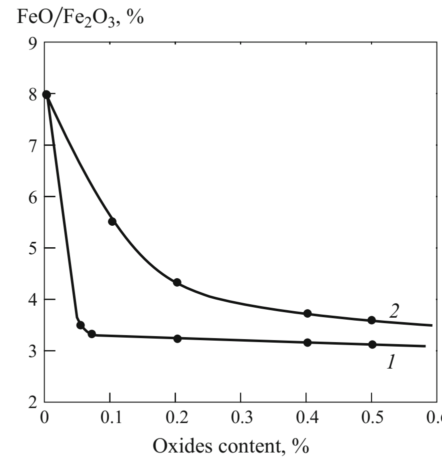

Fig. 2. Curves of the light transmission *T* of crystal glasses containing chromium oxide: *1*) initial; *2*) decolorized NiO; *3*) decolorized Er_2O_3 and Nd_2O_3.

alkali components (K_2O and Na_2O) which increase the water resistance of the crystal, find the optimal production range for a given composition of the glass, and create the possibility of picking decolorizing additives. On this basis new compositions of crystal glasses with complete exclusion of potash from the mix compositions have been developed. The required optical and technological properties are obtained.

It should be especially underscored that in this case it is possible to eliminate lead oxide completely from the glass composition or decrease its content to limits which assure the industry acceptable regimes of production, decoration, and polishing. It is much simpler and cheaper to solve the problem of decolorizing glass if a small amount of PbO (3 – 12%) is present in the glass. In addition, solarization of glass — change of the color tone by exposure to sunlight — is eliminated even with small amounts (2 – 3%) of PbO [5].

New mixes of chemical and physical decolorizers have been developed using rare-earth and variable-valence elements with complete elimination of toxic components. The compositions are represented by the oxide combinations $CeO_2 + NiO$, $CeO_2 + Er_2O_3$, $CeO_2 + Er_2O_3 + Nd_2O_3$, $CeO_2 + Co_2O_3 + Er_2O_3$ and others in a wide concentration range, depending on the basic composition of the glass and the quality and quantity of the coloring impurities [4]. The compositions presented are based on the use of CeO_2 as a chemical decolorizer which replaces arsenic and antimony oxides.

The use of CeO_2 is based on its higher oxidizing power as compared with arsenic oxides, conventionally used in the production of crystal glass. Figure 3 shows the comparative data on decolorization of crystal glass using arsenic oxide and cerium dioxide. The data show that CeO_2 as an oxidizer has an advantage over arsenic oxide. However, its fining power is somewhat lower. This can be explained by the high-temperature decomposition of CeO_2, so that when arsenic oxide is replaced with cerium dioxide the temperature

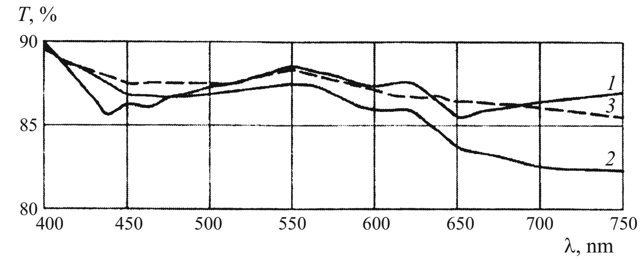

Fig. 3. The dependence of the ratio of iron oxides on the additions of CeO_2 (*1*) and As_2O_3 (*2*).

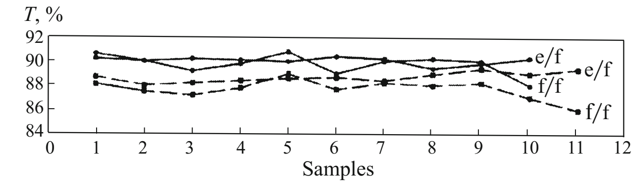

Fig. 4. Light transmission *T* of glasses made in electric (e/f) and flame (f/f) furnaces: ——) total light transmission; – – – –) light transmission at $\lambda = 900$ nm.

in the fining zone must be raised by 15 – 20°C or an additional fining agent must be introduced.

The problem of fining and decolorization of lead crystal glass using cerium dioxide can be solved more effectively with an innovative technology — electric founding of crystal glass. We have studied the change of the light-transmission of crystal glass made in flame and electric furnaces. Analysis showed the total content of iron oxides to be stable and equal to 0.022%. Comparing the oxidative potential of mixes, it should be noted that in the case of electric founding the content of oxygen-containing components was decreased (red lead by 4%, saltpeter by 83%, chemical oxidizer by 50%). At the same time the integral and light transmission at wavelengths characteristic for Fe^{2+} (900 nm) are higher than for glasses made in an electric furnace as compared with flame founding (Fig. 4). The curve for Fe^{2+} is more even in time, which makes it possible to judge the stabilization of the content of this ion in glass during electric founding. Thus, a definite oxidation-reduction state of the melt is attained quite rapidly, the effect of the gas medium is eliminated, and even though the decrease of the oxygen potential of the mix is substantial the total light transmission of the glass increases.

When converting to a composition for lead-free crystal glass it is important to use high-quality raw materials. From this standpoint even quartz sands from the Novoselovskoe deposit with iron impurity content 0.012% do not meet the requirements for quartz sand for obtaining high-transparency glass. For this reason the search for new, pure, raw materials is now an urgent problem.

It should be recalled that the Saratov Technical-Glass Works has had positive experience using in the production of high-grade and crystal glass quartz raw material with iron impurity content 0.008 – 0.010%.

Calcium borate can be used in the successful production of low-lead crystal glasses; this is a complex raw material that makes it possible to introduce CaO and B_2O_3 simultaneously in the ratio 1.64 : 2, respectively. The supply of calcium- and magnesium-containing materials on the raw-materials market has increased substantially in recent years with deliveries of chemically precipitated copper, higher-purity dolomite, including imported, containing 0.007% – 0.03% iron oxide. In addition, various nitrates and other chemically precipitated products with high purity can be used in new compositions without degrading the ecology of production. For example, up to 6 – 8% CaO can be introduced using the new raw materials to produced crystal glass; this makes it possible to maintain the required oxygen potential of the glass and to obtain high optical properties together with improved ecological indicators.

Only a combination of oxides and raw materials that makes it possible to attain iron oxide impurity content at the level present in crystal glass, which will greatly increase the optical characteristics of the glass, should be used in sodium-calcium-silicate compositions.

Thus, the range of high-quality glass composition is greatly expanded and refined for different forms of production in accordance with the production, working, and decoration methods used.

Requirements are increasing for entry monitoring of raw materials, using modern methods of analysis or raw materials and glass, and monitoring the oxygen potential of the mix and glass in the technological production process. The methods and apparatus used for monitoring are well known but once again some plants are not hurrying to increase the level of technical equipping of their laboratories.

In connection with the demand for high-quality raw materials, there is interest in methods for obtaining on a commercial scale pure amorphous mixes — products of hydrothermal reprocessing [6].

The use of cullet merits a special discussion. Only recyclable cullet is used in the production of crystal glass and high-transparency sodium-calcium-silicate glasses. The organization of proper collection, storage, crushing, and shipment of cullet to the hopper characterizes the degree of technological discipline at a plant. The returnable cullet must not be contaminated with iron-containing, organic, and other impurities. But the introduction of cullet in amounts from 20 to 40 – 50% into the production of high-grade and crystal glasses always decreases the oxygen fraction proportionately. Cullet is a reducer and shifts the oxidation-reduction equilibrium of iron oxides in the direction of FeO formation — the more intensely coloring form: Fe^{3+} (cullet) $\to$ Fe^{2+} (light blue tone in the glass). For this reason, under industrial conditions the oxygen potential must be stabilized by adjusting the introduction of oxidizers on the basis of calculations or the cullet fraction introduced must be stabilized.

To develop technological production specifications manufacturing plants must now analyze the production process

and eliminate the possibility of contamination of raw materials and disruptions of the technological regime that can lower the light transmission of glass.

For example, one plant which produces articles made from high-grade glass has converted to high-quality glass compositions with complete elimination of lead oxide without shutting down the glassmaking furnace. Glasses in which the total visible-range transmission is practically the same as in lead glasses and equals 89 – 89.5% were obtained. The use of expensive and contaminated potash has been completely eliminated; a stable and inexpensive physical decolorizer is used. The composition of the glass is suitable for manual and automated production.

In summary, the work performed on the reduction of the cost of molten glass in high quality production at glass works should be done with the links in the production cycle strictly tied together: composition – properties – raw material resources – technology – ecology – economics.

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